

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : C08J 9/32, C08L 63/00 H01Q 15/14, C08K 7/00		A1	(11) International Publication Number: WO 85/ 05113 (43) International Publication Date: 21 November 1985 (21.11.85)
<p>(21) International Application Number: PCT/US85/00625</p> <p>(22) International Filing Date: 9 April 1985 (09.04.85)</p> <p>(31) Priority Application Numbers: 607,847 609,178</p> <p>(32) Priority Dates: 7 May 1984 (07.05.84) 11 May 1984 (11.05.84)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant: HUGHES AIRCRAFT COMPANY [US/ US]; 200 North Sepulveda Boulevard, El Segundo, CA 90245 (US).</p> <p>(72) Inventors: DuPONT, Preston, S. ; 9046 Bertrand Avenue, Northridge, CA 91325 (US). FREEMAN, Janet, E. ; 129 North Bonnie Avenue #1, Pasadena, CA 91106 (US). RITTER, Robert, E. ; 741 Cloyd Road, Palos Verdes Estates, CA 90274 (US). WITTMANN, Alois ; 29017 Geronimo Drive, Palos Verdes, CA 90274 (US). OLDHAM, Susan, L.; 3472 Heather Road, Long Beach, CA 90808 (US).</p>			
<p>(74) Agents: LACHMAN, Mary, E. et al.; Hughes Aircraft Company, Post Office Box 1042, Bldg. C2, M.S. A126, El Segundo, CA 90245 (US).</p> <p>(81) Designated States: AU, DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, SE (European patent).</p> <p>Published <i>With international search report.</i></p>			

(54) Title: FIBER-REINFORCED SYNTACTIC FOAM COMPOSITES AND METHOD OF FORMING SAME

(57) Abstract

Fiber-reinforced syntactic foam composites having a low specific gravity and a low coefficient of thermal expansion suitable for forming lightweight structures for spacecraft applications are prepared from a mixture of a heat curable thermosetting resin, hollow microspheres having a diameter of about 5 to 200 micrometers and fibers having a length less than or equal to 250 micrometers.

-1-

FIBER-REINFORCED SYNTACTIC
FOAM COMPOSITES
AND METHOD OF FORMING SAME

1

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates, in general, to syntactic foam composites and, more particularly, to fiber-reinforced thermosetting resin based syntactic foam composites exhibiting a low specific gravity and a low coefficient of thermal expansion.

10 2. Description of the Prior Art

A continuing objective in the development of satellites is to optimize satellite payload weight. One means of achieving this objective is to reduce the intrinsic weight of various operational elements within the spacecraft. It has been recognized by the art that the desired weight reduction could be realized by replacing conventional materials, such as aluminum, with lower density synthetic composites possessing requisite mechanical, thermal and chemical stability. Included in these low density synthetic composites is a group of materials referred to in the art as syntactic foams.

1 can be achieved, as well as reducing dimensional
stability. If syntactic foam systems are too highly
filled, sacrifices are made in moldability, coefficient
of thermal expansion, strength, density, dimensional
5 stability and stiffness. Moreover, such foams tend to
exhibit poor adhesion to metallic plating which is
required to form the desired product, such as an antenna
component.

10 In order for the syntactic foam to be useful
as a substitute for aluminum in antenna and antenna
microwave components in a spacecraft, the foam must
have the following characteristics.

15 (1) The material must have a specific gravity
of 1.00 or less, as compared to a specific gravity
of 2.7 for aluminum.

20 (2) The material must have a linear coefficient
of thermal expansion (α or CTE) comparable
to that of aluminum, preferably close to
 13×10^{-6} in/in/ $^{\circ}\text{F}$ (23×10^{-6} cm/cm/ $^{\circ}\text{C}$) or less.
Thermal distortion of antenna components subjected
to thermal cycling in the extremes of the space
environment is a major contributing factor to
gain loss, pointing errors, and phase shifts.

25 (3) The material must meet the National
Aeronautics and Space Administration (NASA)
outgassing requirements to insure that the
material does not release gaseous component
substances which undesirably accumulate on other
spacecraft parts in the outer-space vacuum.

30 (4) The material must have long-term
stability, as required for parts exposed to the
space temperature environment (e.g., -100 $^{\circ}\text{F}$ to
250 $^{\circ}\text{F}$ or -73 $^{\circ}\text{C}$ to 121 $^{\circ}\text{C}$) for extended periods of
time, such as 10 years.

1 bonded together by the heat cured resin matrix. The
composites of the present invention readily meet the
specific gravity, coefficient of thermal expansion and
NASA outgassing requirements, which easily qualify the
5 composites as aluminum substitutes for spacecraft use.

DETAILED DESCRIPTION OF THE INVENTION

In order to form the fiber-resin-microsphere composite of the present invention having the desired density and coefficient of thermal expansion, each of the three components must be selected so that the resulting combination thereof provides a mixture amenable to being cast into the desired configuration, as well as providing a final product having the required structural and physical properties. Acceptable mixtures must have a viscosity that produces an accurate, void-free casting with uniform material properties. In addition, the proportion of fiber in the composite must provide the required thermal expansion, strength, and stiffness properties. Further, the microsphere component must be chosen to provide the required low density in the composite. Finally, each of the components must be capable of being combined with the other components and the effect of each on the other in the mixture thereof, as well as in the final composite must be taken into account. In particular the properties of the composite are influenced by the properties, relative volume ratios, and interactions of the individual components. More specifically, density, strength, stiffness (brittleness), coefficient of thermal expansion and processibility are strong functions of filler and fiber type, volume ratios and micropacking. The following discussion provides a more detailed consideration of these various factors. It should be noted that in the

1 practice of the present invention are epoxy resins
having 1,2 epoxy groups or mixtures of such resins,
and include cycloaliphatic epoxy resins such as the
glycidyl ethers of polyphenols, liquid Bisphenol-A
5 diglycidyl ether epoxy resins (such as those sold
under the trademarks Epon 815, Epon 825, Epon 828 by
Shell Chemical Company), phenolformaldehyde novolac
polyglycidyl ether epoxy resins (such as those sold
under the trademarks DEN 431, DEN 438 and DEN 439 by
10 Dow Chemical Company), and epoxy cresol novolacs (such
as those sold under the trademarks ECN 1235, ECN 1273,
ECN 1280 and ECN 1299 by Ciba Products Company).

The particular epoxy resins preferred in the
practice of the present invention are polyglycidyl
15 aromatic amines, i.e. N-glycidyl amino compounds prepared
by reacting a halohydrin such as epichlorohydrin with
an amine. Examples of the most preferred polyglycidyl
aromatic amines include diglycidylaniline, diglycidyl
orthotolidine, tetraglycidyl ether of methylene dianiline
20 and tetraglycidyl metaxylene diamine, or mixtures
thereof.

The epoxy resins which are preferably in liquid
form at room temperature are admixed with polyfunctional
curing agents to provide heat curable epoxy resins
which are cross-linkable at a moderate temperature,
25 e.g., about 100°C, to form thermoset articles. Suitable
polyfunctional curing agents for epoxy resins include
aliphatic polyamines of which diethylene triamine and
triethylene tetramine are exemplary; aromatic amines of
30 which methylene dianiline, meta phenylene diamine,
4,4' diaminodiphenyl sulfone are exemplary; and
polycarboxylic acid anhydrides of which pyromellitic
dianhydride, benzophenone tetracarboxylic dianhydride,
hexahydrophthalic anhydride, nadic methyl anhydride
35 (maleic anhydride adduct of methyl cyclopentadiene),

1 A particularly useful resin composition for
forming the composites of the present invention comprises
a polyglycidyl aromatic amine, a polycarboxylic acid
anhydride curing agent, and a curing accelerator.
5 Examples 3 and 4 herein are directed to the use of
this preferred resin formulation in the practice of
the present invention.

2. Hollow Microspheres

10 The syntactic foam composites prepared in accordance
with the present invention contain a relatively uniform
distribution of hollow microspheres. These hollow
microspheres are usually hollow thermoplastic spheres
composed of acrylic-type resins such as polymethyl-
methacrylate, acrylic modified styrene, polyvinylidene
15 chloride or copolymers of styrene and methyl methacrylate;
phenolic resins; or hollow glass, silica or carbon spheres
that are very light in weight and act as a lightweight
filler in the syntactic foam. These microspheres
preferably have a diameter in the range of about 5 to
20 about 200 micrometers. Methods for the production of
these hollow microspheres are well known in the art
and are discussed, for example, by Harry S. Katz and
John V. Milewski in the book entitled, "Handbook of
25 Fillers and Reinforcements for Plastics," Chapter 19:
Hollow Spherical Fillers, Van Nostrand Reinhold, 1978,
the teachings of which are incorporated herein by
reference. Such microspheres are readily available
commercially. These hollow microspheres can be
30 compressed somewhat when subjected to external pressure.

1 "Carbosphere" carbon microspheres available from the
Versar Corporation have a specific gravity of 0.32 and
a mean diameter of 50 micrometers. Desirably, a mixture
5 of two or more types of hollow microspheres may be
employed in the practice of the present invention. The
glass microspheres provide the syntactic foam with
improved structural strength, while those of carbon
advantageously contribute to both a lowered coefficient
10 of thermal expansion and greater amenability to subsequent
metal-plating operations. When using a combination of
glass and carbon microspheres in preparing the composites
of the present invention, the ratio of glass microspheres
to carbon microspheres is about 1:4 to 1:1.

15 Furthermore, it has been found by using packing
theory that an increased volume percent solids in the
resin mixture can be achieved. Packing theory is based
on the concept that, since the largest particle size
filler in a particular reinforcement system packs to
produce the gross volume of the system, the addition of
20 successively smaller particles can be done in such a
way as to simply occupy the voids between the larger
filler without expanding the total volume. This theory
is discussed by Harry S. Katz and John V. Milewski, in
the book entitled "Handbook of Fillers and Reinforcements
25 for Plastics," Chapter 4. Packing Concepts in Utilization
of Filler and Reinforcement Combinations, Van Nostrand
Reinhold, 1978. The fillers used in the present
invention are chosen on the basis of particle size,
shape, and contribution to overall composite properties.
30 This theory applies to the use of solid particulates as
well as hollow spheres. Because of the high viscosity
of such a highly loaded resin, the mixture could not
flow into the mold without damaging the microspheres.

1 mixture at a given level of viscosity, which provides a
higher level of reinforcement at that viscosity level
by shorter fibers. In addition, the use of shorter
fibers improves the uniformity of the mix. Thus,
5 fibers useful in the composite of the present invention
have a length less than or equal to 250 micrometers
and generally in the range of about 50 to about 250
micrometers. Fibers having a length about 150 to
about 250 micrometers were found to provide the best
10 compromise between viscosity and reinforcement as
discussed previously. When graphite fiber, the preferred
fiber material, is used, the diameter of the graphite
fibers is in the range of about 5 to about 10 micrometers.

Moreover, the interaction of the fibers with the
15 microspheres discussed previously must be considered.
It has been determined by micropacking theory, as
described in Chapter 4 of the book by Katz and Milewski,
previously referenced, that the optimum ratio of fibers-
20 to-spheres varies with the length/diameter ratio (L/D)
of the fibers and with the ratio of the sphere-diameter
to the fiber-diameter (R). For each value of L/D,
there is one R value where the packing efficiency is
zero; and as R increases or decreases on either side of
this minimum, packing efficiency increases. It has
25 been found most desirable in the practice of the present
invention to use graphite fibers of the micrometer
lengths discussed above, which have a length to diameter
ratio (L/D) of about 5:1 to about 30:1 and preferably
about 15:1 to about 30:1, and a sphere-diameter to
30 fiber-diameter ratio (R) of at least about 6:1 and
preferably about 15:1.

Graphite fibers used in the practice of the
present invention are selected to have high strength
and low density. Celanese GY-70 graphite fiber and
35 Courtaulds HM-S graphite fiber are especially suitable.

1 titanate coupling agent such as di(dioctylpyrophos-
phato)ethylene titanate (KR238M available from Kenrich
Petrochemical Company of Bayonne, New Jersey); or
5 tetra(2,2 diallyloxyethyl-1-butoxy)titanium di(ditridecyl
phosphite) (KR55 available from Kenrich); or titanium
di(cumylphenylate) oxyacetate (KR134S available from
Kenrich); or isopropyl tridodecylbenzenesulfonyl
10 (KR9S available from Kenrich). The coupling agents
enable the resin to wet the sphere and fiber surfaces, and
promote a stronger bond between the resin, microspheres,
15 and fibers without increasing the viscosity appreciably.

The coupling agents may be applied by simply
dissolving the agents in the resin-microsphere-fiber
blend. Optionally, these agents may be applied by
15 first dissolving the agents at a concentration of
0.1 - 0.5% of the filler weight in water or an organic
solvent such as isopropanol or Freon TE (a fluorocarbon
compound available from E.I. Dupont and Company); and
then immersing the microspheres and fibers which have
20 been premixed in predetermined proportions in the
solution for a period of 5 to 30 minutes, followed by
filtering and drying the mixture. The microsphere-fiber
mixture may then be blended with the heat curable resin
preparatory to fabricating the syntactic foam composite.

25

4. Optional Microbeads

Solid microbeads may optionally be incorporated
in the composite of the present invention in order to
increase packing efficiency. Advantageously, such
30 microbeads were also found to decrease the viscosity of
the formulation, improve its pourability, and increase
composite uniformity. In a preferred practice of the
present invention, about 2 to about 8 percent by volume
of solid inert material, such as glass or silica micro-
35 beads having a diameter of about 2 to about 8 micrometers

1 at which the resin is curable, e.g. to 250°F to 350°F
10 (121°C to 177°C), for epoxy resins generally and about
150°F to 250°F (66 to 121°C) for the preferred epoxy
composition described herein, at 50 to 100 psi (2586 to
5 5171 mm Hg or 7.25 to 14.5×10^{-3} Pa) for about 2 to
about 4 hours.

Molding of the filled heat curable resin formulations to form syntactic foam composites of the present invention may also be effected by other conventional molding methods including transfer molding and compression molding procedures wherein the heat curable formulation is cured at the above-noted curing temperatures, using pressures on the order of 800 to 1000 psi (41372 to 51715 mm Hg or 0.116 to 0.145 pascals) for 1 to 2 hours.

15 It has been found particularly advantageous to form the filled heat curable resin mixtures into the syntactic foam composites of the present invention by a vacuum liquid transfer molding process. In this procedure, the mold is first loaded with the microsphere/fiber filler which has been mechanically or manually premixed in predetermined proportions and pretreated with a sizing agent as previously described. Next, the mold may optionally be vibrated to promote a uniform distribution of the filler in the mold (e.g. about 5 minutes on a vibration table). Then the mold cavity is filled with the heat curable resin. The mold is a sealable pressure vessel constructed to support the vacuum/pressure sequence described below. To prepare for the molding process, the mold cavity is preheated to bring the cavity up to the temperature at which the heat curable resin is curable. A vacuum is then drawn on the mold to degas the mold cavity contents and to impregnate the filler with the resin. The vacuum is released to atmospheric pressure to

1 that of aluminum or steel. Depending on the filler
fiber volume used in the composite of the present
invention, composites may be tailored to have coefficients
of thermal expansion ranging from that of the unfilled
5 resin to that of steel.

Because of their relatively low coefficient of
thermal expansion, epoxy resin based syntactic foam
composites prepared in accordance with the present
invention have been determined to be especially amenable
10 to conventional metal plating processes, such as electro-
less plating, when the surfaces thereof are prepared
for plating by plasma treatment. The relatively high
adhesion of metal deposits to the surface of the present
composite is believed to be a function of both the
15 topography of the plasma-treated surface plus the
mechanical integrity of the remaining surface. The
plasma removes the resin "skin" from the composite,
leaving the graphite fiber/microballoon filler exposed,
20 to provide a surface which is readily platable. Such
metal plating of the composite of the present invention
may be required in forming antenna components in which
an electrically conductive surface or path is required,
as is known in the art.

To effect plasma treatment in preparation for
25 plating, the surface of the filler reinforced epoxy
resin based composite is subjected to a plasma process
with a reaction gas containing a mixture of air, nitrogen,
or argon with oxygen, water vapor, nitrous oxide, or
other resin oxidizing source, to remove the polymer
30 "skin" and expose the filler, as discussed above.
Normal plasma etching conditions known to the art are
used. For example, for a plasma excitation energy of
200 watts/ ft^2 of composite, an O_2 /inert gas source
of approximately 1000 ml/minute, a vacuum pressure of
35 200 micrometers Hg, and one hour duration are used.

1 Next, a copper plating is built up to any desired
thickness on the electroless copper by known electrolytic
plating methods, using commercially available electro-
deposit copper plating solution. Finally an electrolytic
5 silver plate is formed to the desired thickness on the
electrolytic copper plate by known methods, using
commercially available silver plating solution formula-
tions. Silver plating of a composite of the present
invention is described in Example 5.

10

The following examples illustrate but do not limit
the present invention.

15

EXAMPLE 1

This example illustrates a process for forming
one type of fiber-reinforced syntactic foam composite
in accordance with one process embodiment of the present
invention.

20

The components of the syntactic foam formulation
designated "S-61" are shown in Table I. The following
details regarding the components of S-61 apply to Table I.

- a. MY720 is a tetraglycidyl methylene dianiline
manufactured by Ciba Geigy.
- b. HY906 is a nadic methyl anhydride hardener
manufactured by Ciba Geigy.
- c. BDMA is benzylidimethylamine accelerator
available from E.V. Roberts or Ciba Geigy.
- d. D32/4500 microspheres are borosilicate
microspheres having a mean diameter of 75
micrometers, a specific gravity of 0.32, and a
compressive strength of 4500 psi, available from
the 3M Company.

30

35

Preparation of Graphite Fibers

1 The GY70 graphite fibers in continuous tow form
were cut into lengths of approximately 1/8 inch to 1/2
inch (0.32 to 1.27 centimeters), using a paper cutter.
5 Batches of the chopped fibers (approximately 80 grams
each) were loaded into a ball mill jar having a one-
gallon capacity and sufficient Freon TF was added to
cover the ceramic balls to serve as a suspension medium.
The fibers were milled for 24 hours. Scanning electron
10 micrographs of the milled fibers showed them to be
broken into small fragments ranging from approximately
2 to 10 micrometers in length.

15 The milled fibers and Freon were poured into a
shallow stainless steel pan, and the Freon was allowed
to evaporate. The fibers were then dried 4 hours in an
air-circulating oven set at 250°F (121°C) and sifted
on a vibration plate to pass a 325 mesh screen. The
dried, sifted fibers were stored in a desiccator box
until ready for use.

20

Composite Formation

25 The formulation S61 was prepared as follows. A
one-gallon hot/cold pot for a Waring blender was heated
to 140°F (60°C) using a temperature-controlled water
bath. The premeasured amount of the HY906 hardener was
put in the blender and the mixer speed was adjusted
using a Variac variable potentiometer so that the
hardener was just barely agitated. With the blender on
"low" setting, the Variac was turned to 70 percent of
30 full speed. The resin, which had been preheated to
160°F (71°C), was added to the pot and the contents of
the pot were mixed until the mixture appeared homogeneous
(about 5 minutes), and then cooled to room temperature.

1 placed in an oven preheated to 275°F (135°C) and a
thermocouple was placed on/in each of the following: on
the mold, in the oven, and in the mold contents through
a hole in the side wall of the mold. When the thermo-
5 couple in the mold contents registered 275°F (135°C),
the following cure cycle was run: 10 minutes at 275°F
(135°C); 10 minutes at 300°F (149°C); 120 minutes at
350°F (177°C). The maximum oven rate was used for
changing temperatures.

10 The mold was removed from the oven and was
disassembled, and the part was removed from the mold
while the mold was still hot, being sure to keep the
thermocouple embedded in the syntactic foam. The part
was deflashed as necessary with a file. For the post-
cure, the demolded part was placed in an oven preheated
15 to 400°F (204°C) between 0.5 inch thick aluminum plates,
with 2-5 kilograms weight on the top plate. When the
thermocouple in the syntactic foam registered 400°F
(204°C), the following post-cure cycle was run: 1 hour
at 400°F (204°C); 1 hour at 425°F (218°C); 1 hour at
450°F (232°C), and 1 hour at 475°F (246°C) Finally, the
20 part was removed from the oven.

25 The fiber reinforced syntactic foam composite
formed as described above was found to have the properties
shown in Table II. With regard to Table II, the
following test requirements apply:

- a. CTE was determined using a quartz
dilatometer to measure the change in
length as a function of temperature.
- b. Specific gravity was measured using a
pycnometer.
- c. Viscosity was measured with a Brookfield
Viscometer.

1

EXAMPLE 2

This example illustrates a process for forming fiber-reinforced syntactic foam composites of various compositions in accordance with the present invention.

5

The components of the various formulations designated as the "RSF series" are shown in Table III. The following details regarding the specific components apply to Table III.

10

a. Epoxy is a mixture of 70 parts Glyamine 135 (diglycidyl ortho toluidine) and 30 parts Glyamine 120 (tetraglycidyl methylene dianiline), both materials obtained from FIC Resins of San Francisco, California, mixed with about 115 parts nadic methyl anhydride hardener and about 0.25 parts benzylidimethyl-aniline accelerator.

20

b. Zeeospheres 0/8 are solid glass spheres having a median diameter of 3 micrometers, available from Zeelan Industries of St. Paul, Minnesota.

25

c. Carbospheres Type A are hollow carbon spheres having an average diameter of 50 micrometers, available from Versar of Springfield, Virginia.

d. 3M A 32/2500 glass bubbles are glass microspheres having a mean diameter of 50 micrometers, a specific gravity of 0.32, and a compressive strength of 2500 psi, available from the 3M Company of Minnesota.

30

e. 3M A 16/500 are glass microspheres having a mean diameter of 75 micrometers, a specific gravity of 0.16, and a compressive strength of 500 psi, available from the 3M Company.

35

f. Eccospheres SI are hollow silica microspheres having a diameter of 45-125 micrometers, available from Emerson and Cuming Inc. of Canton, Massachusetts.

- 1 a. Density was determined by pycnometer.
- b. CTE was determined using a quartz dilatometer to measure the change in length (Δl) as a function of temperature.
- 5 c. Compressive strength was determined using the American Society for Testing and Materials (ASTM) Standard No. D695.
- d. Compressive modulus was determined using ASTM D695, using crosshead speed in place of strain guages.
- 10 e. Uniformity was determined by visual inspection.
- f. Viscosity was measured with a Brookfield viscometer.

15

20

25

30

35

TABLE IV

PROPERTIES OF COMPOSITES OF FORMULATIONS OF RSF SERIES

RSF-FORMULATION	DENSITY (g/cc)	CTE (10 ⁻⁶ in/in/°F)	COMPRESSIVE STRENGTH (psi)*	COMPRESSIVE MODULUS (10 ³ psi)*	UNIFORMITY (1-10)	VISCOSITY
3	0.898	16.82	15,300	394	3.7	5
4	0.881	13.81	16,300	447	4.3	4
5	0.872	15.10	16,400	406	4.0	4
6	0.869	22.16	14,300	407	3.5	5
7	0.968	20.82	15,100	394	2.7	8
8	0.982	21.39	18,400	410	4.7	7
13	1.000	25.46	14,900	386	2.3	7
14	1.019	25.55	15,400	405	1.8	6
19	0.852	14.06	13,200	411	4.0	3
20	0.694	14.09	8,600	335	2.7	2
21	0.8561	17.02	14,000	439	3.4	3
23	0.9912	20.69	16,300	384	5.5	7
25	1.0387	30.51	19,000	423	--	6
26	1.005	21.73	15,700	395	7.3	5
28	0.982	20.10	17,100	411	6.5	5
29	1.002	20.70	17,800	393	7.6	5
31	0.888	23.90	17,800	400	6.6	8
33	0.815	23.10	13,300	343	3.9	7
34	0.824	14.59	17,500	394	4.4	6
34F	0.842	14.24	17,300	425	--	--
35	0.738	17.23	10,200	303	4.0	6
36	0.745	17.14	12,100	335	3.0	5

* 1 psi = 1.45 × 10⁻⁴ pascals

	<u>Filler Component</u>	<u>WT. (gms.)</u>
	Carbosphere, 50 micrometers	50
	HM-S fiber, 50 micrometers	50
5	Titanate sizing agent KR238M	1

Using the above-noted resin and filler, each of a series of resin/filler formulations shown in Table V was processed as described below in order to form the composite of the present invention.

The filler composition (i.e. a mixture of the fibers and microspheres pretreated with the sizing agent as previously described herein) was loaded into a cleaned 5.5 inch x 0.5 inch (14cm x 1.3cm) wide slab mold internally coated with a polyvinyl alcohol release agent. The mold was preheated to 212°F (100°C), the temperature at which hardening of the heat curable epoxy resin formulation was initiated. The epoxy resin formulation was poured into the mold containing the filler. The mold was placed in a laminating press, a nylon vacuum bag was constructed around the compression tooling of the press, and a vacuum pressure of 125 millimeters (mm) mercury pressure (166,625 pascals) was maintained on the assembly for 2 minutes to draw down the resin to impregnate the filler and to degas the resin materials in the mold. The vacuum was then released without removal of the vacuum bag and the assembly held in this passive vacuum state for an additional 2 minutes. Thereafter, a constant positive pressure of approximately 800 pounds per square inch (41,360 mm Hg or 5.5×10^6 pascals) was imposed on the resin/filler mixture in the mold for 2 hours at 212°F (100°C). During this pressurization stage, the resin was bled from the mold in the amount noted in Table V.

TABLE V
COMPONENTS OF MOLDING COMPOSITION

Specimen No.	Resin (gms.)	Filler (gms.)	Filler Ratio		Resin Bleed During Molding %
			(Wt.%)	(Vol.%)	
1	40	10	45	64	69.2
2	30	9.4	38	57	47.8
3	30	9.4	38	57	47.9
4	17.0*	5.5	37	57	45.3
5	19.0*	6.0	39	59	50.6
6	20.7*	6.5	41	60	54.6

* KRL34S sizing agent was substituted for the previously noted sizing agent.

$$** \text{ Resin bleed} = \left(\frac{W_1 - W_2}{W_1} \right) \cdot 100$$

where W_1 = initial resin weight

W_2 = resin displaced from the mold, using a bleeder cloth.

Vol. % calculated from resin bleed varies about 10-20% of the actual vol. % value.

EXAMPLE 4

1 This example illustrates the formation of composites
as set forth in Example 3 with the exception that the
composition of the filler formulation was varied. The
5 procedure set forth in Example 3 was followed except
that the filler compositions shown in Table VII were
used. The following details regarding the specific
components apply to Table VII.

10 a. Carbospheres are carbon microspheres having
 a specific gravity of 0.32 and a mean diameter
 of 50 micrometers, available from Versar
 Corporation.

15 b. HM-S 50 (50 μ) graphite fibers are graphite
 fibers having a length of about 50 micrometers
 and a diameter of about 8 micrometers, available
 from the Courtaulds Co. of the United Kingdom.

20 c. 1/4 mm HM-S 50 graphite fibers are graphite
 fibers having a length of about 250 micrometers
 and a diameter of about 8 micrometers,
 available from the Courtaulds Co. of the
 United Kingdom.

25 d. C15/250 glass microballoons are composed of
 borosilicate glass, have a diameter of 10-200
 micrometers, a density of 0.15 gm/cm³, and
 a compressive strength of 250 psi, available
 from the 3M Company of Minnesota.

30 The physical properties of the molded composite
 slabs so formed are set forth in Table VIII.

1

TABLE VIII

PHYSICAL PROPERTIES OF MOLDED COMPOSITE SLABS

5

10

Filler Used in Molded Sample	Thickness (in.)	Density (gm/cm ³)	Filler Ratio		Resin Bleed %	Cu Coating Removed
			(Wt.%)	(Vol.%)		
A	0.443	1.050	39	59	51.0	≤ 5%
B	0.540	0.753	26-47	56-77	61.9	≤ 5%
C	0.850	0.948	27	54	16.2	5-15%

15

20

In addition, the surfaces of the molded composite slabs of Table VIII were then subjected to plasma treatment under the following conditions: O₂/inert gas source of approximately 1000 ml/minute, vacuum pressure of 200 μ Hg, and one hour duration. The surfaces of the plasma etched slabs were then copper plated to a thickness of about 3-4 mils by dipping the etched slabs in an aqueous Shipley #328 electroless copper plating bath.

25

The plated composite was then evaluated for adhesion of the deposited copper layer using the ASTM D3359 tape adhesion test and thermal shock cycle of Example 3. The adhesion results are recorded in Table VIII, indicating the amount of copper coating on lattice removed by the tape.

30

35

1 requirements for use in space applications. Syntactic foams plated with metals such as silver and copper may serve as metal-plated core materials for both microwave components and microwave reflectors.

5 The fiber-reinforced syntactic foam composites of the present invention achieve a 3-to-1 reduction in weight in comparison with aluminum, which makes these components attractive for weight-sensitive applications in a spacecraft environment. At the same time, however,
10 in situations calling for high volume production, the readily-moldable nature of the reinforced foam mixture disclosed herein further offers the potential of significantly reduced cost in comparison with the machining traditionally employed for the production of conventional
15 metal parts.

The preceding description has presented in detail exemplary preferred ways in which the concepts of the present invention may be applied. Those skilled in the art will recognize that numerous alternatives encompassing many variations may readily be employed without departing from the intention and scope of the invention set forth in the appended claims. In particular, the present invention is not limited to the specific resin, fibers, or microballoons set forth herein as examples. By following the teachings provided herein relating to the effect of each component of the mixture on the final composite and the effect of the various components on each other, other suitable resin, fiber, and microballoon materials may readily be determined. Further, by following the teachings provided herein, it may be determined how to form composite materials having a density or coefficient of thermal expansion other than those set forth herein as required for the specifically mentioned end use in space applications.

1 5. The composite of Claim 3 wherein the polyfunctional curing agent is a polyamine, a polycarboxylic acid anhydride, or the maleic anhydride adduct of methyl cyclopentadiene.

1 6. The composite of Claim 3 wherein the mixture further comprises benzylidimethylaniline as an accelerator.

1 7. The composite of Claim 1 wherein the hollow microspheres are formed of glass, silica, carbon, acrylate resins, or phenolic resins.

1 8. The composite of Claim 7 wherein the hollow microspheres are formed of glass and have an average diameter of about 50 micrometers.

1 9. The composite of Claim 7 wherein the hollow microspheres comprise a mixture of glass microspheres and carbon microspheres.

1 10. The composite of Claim 1 wherein the fibers are formed of graphite, glass, carbon, nylon, or polyamide.

1 11. The composite of Claim 10 wherein the fibers are formed of graphite and have a length of about 50 micrometers and a diameter of about 8 micrometers.

1 18. The composite of Claim 16 wherein the
polycarboxylic acid anhydride is present in sufficient
quantity to react with from about 60 to about 90 percent
of the epoxide groups in said polyglycidyl aromatic
5 amine.

1 19. The composite of Claim 16 wherein the
polycarboxylic acid anhydride is nadic methyl anhydride,
methyl tetrahydrophthalic anhydride, or methyl
hexahydrophthalic anhydride.

1 20. The composite of Claim 16 wherein said curing
accelerator is present in the amount of about 0 to
about 3 percent, by weight.

1 21. The composite of Claim 16 wherein said curing
accelerator is 2-ethyl-4-methyl imidazole or stannous
octoate.

1 22. The composite of Claim 16 wherein:
a) said uncured polyglycidyl aromatic amine
is diglycidyl orthotolidine and is present in the
amount of about 100 parts per hundred resin by weight;
5 b) said curing agent is nadic methyl anhydride
and is present in the amount of about 100 parts per
hundred resin by weight; and
c) said curing accelerator is 2-ethyl-4-
methyl imidazole and is present in the amount of about
10 2 parts per hundred resin by weight.

1 25. A fiber-reinforced syntactic foam composite
as set forth in Claim 1, comprising:

5 a) a heat curable thermosetting epoxy
resin comprising a mixture of tetraglycidyl methylene
dianiline, nadic methyl anhydride, and benzylidimethyl-
aniline;

10 b) hollow glass microspheres having a mean
diameter of about 75 micrometers; and

10 c) graphite fibers having a length of about
150 micrometers and a diameter of about 8 micrometers.

1 26. An article of manufacture comprising a body
formed from the composite material of Claim 1.

1 27. The article of manufacture set forth in Claim
26 which further comprises a layer of electrically
conductive material adhered to selected surfaces of the
body.

1 28. The article of manufacture set forth in Claim
27 wherein said article comprises a component in an
antenna structure.

1 29. A method for fabricating a fiber-reinforced
syntactic foam composite as set forth in Claims 1-25,
which comprises the steps of:

5 a) admixing a heat curable thermosetting
resin, hollow microspheres having a diameter in the
range of about 5 to about 200 micrometers and fibers
having a length less than or equal to 250 micrometers
to form a mixture of the resin, microspheres and fibers;
and

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 85/00625

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁴: C 08 J 9/32; C 08 L 63/00; H 01 Q 15/14; C 08 K 7/00

II. FIELDS SEARCHED

Minimum Documentation Searched †

Classification System	Classification Symbols
IPC ⁴	C 08 J; C 08 K C 08 L; H 01 Q;

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. 13
A	GB, A, 2058794, (NITTA BERUTO) 15 April 1981, see claims; page 1, lines 53-85; examples	1,2,7,10,12, 26, 29
A	CA, A, 1063747 (J.D.L. TESSIER et al.) 2 October 1979, see claims 1,4; page 4a - page 5, line 2	1,2,7,10,12, 26,29
A	Chemical Abstracts, Volume 89, part 2, 10 July 1978, (Columbus, Ohio, US) see abstract No. 89=7325F & JP, A, 7818647 (SUMITOMO ELECTRIC IN- DUSTRIES)	1-3,5,7,10, 12,26,29
A	GB, A, 1271298 (CIBA-GEIGY) 19 April 1972, see claims 1-8; page 2, lines 50-79; examples I, II; pages 35-124	1
A	FR, A, 2112215 (GRUNZWEIG & HARTMANN) 16 June 1972, see claims 1,2,4,5	26,27,28
A	EP, A, 0102335 (KEMANORD) 7 March 1984,	

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

1th July 1985

Date of Mailing of this International Search Report

17 JUL 1985

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

G.L.M. *Meltz*
Knuwdenberga

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 85/00625 (SA 9453)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/07/85

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2058794	15/04/81	None	
CA-A- 1063747	02/10/79	SE-A-	7608086 31/01/77
GB-A- 1271298	19/04/72	DE-A, B, C FR-A- US-A-	1957114 11/06/70 2030072 30/10/70 3652486 28/03/72
FR-A- 2112215	16/06/72	NL-A-	7103795 05/04/72
EP-A- 0102335	07/03/84	SE-A- JP-A- US-A-	8204595 06/02/84 59047236 16/03/84 4483889 20/11/84